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SPECTRAL DISTRIBUTIONS V. VISIBLE SPECTRA OF  
STANDARD AND IMPROVED GREEN FLARE COMPOSITIONS

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HENRY A. WEBSTER, III

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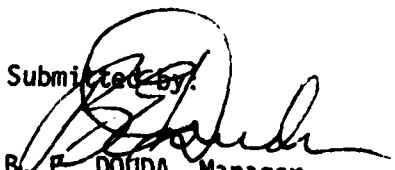
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## PREFACE

The contents of this report were reported at the 1979 Annual Meeting of the Pyrotechnics and Explosives Applications Section of the American Defense Preparedness Association. The meeting was held 7-9 November 1979 at the United States Military Academy, West Point, New York. This document bears Word Processing control number 08976/21.

## INTRODUCTION

The production of a good green colored signal has long been the nemesis of the pyrotechnician. This is especially true if a good green signal is defined as one with not only good color but also a large luminous efficiency. An excellent review of green signals and their associated problems has been given by Jackson, Kaye and Taylor.<sup>1</sup> Green signals currently in use are composed of magnesium, potassium perchlorate, barium nitrate, some chlorine donor (e.g., polyvinyl chloride), other color additives such as copper, and a binder. One standard Navy green flare has a typical output of dominant wavelength ( $\lambda_D$ ) = 562 nanometers (nm), excitation purity = 53%, luminous power (cp) = 20,000 cd, a burn time of 29 seconds and a luminous efficiency of 4300 cd-s/g. In earlier work reported by Jackson, Kaye and Taylor, an improved green signal composed of Delrin® and barium chlorate monohydrate was developed.<sup>1</sup> This flare had  $\lambda_D$  = 552 nm, excitation purity = 78%, luminous power = 320 cd, burn time = 80 seconds (calculated) and luminous efficiency = 170 cd-s/g. Thus this flare has a better color but the color can be obtained only with a large loss in luminous efficiency. In limited field tests under clear night conditions these flares were visible at slant ranges of ten miles.

This report describes the demonstration of new green flare compositions which have shorter dominant wavelengths and increased luminous efficiencies. The visible spectra of the best new green formula and a standard Navy green flare are presented and analyzed.

- 
1. B. Jackson, S. M. Kaye, and F. R. Taylor, Improved Green Signal Compositions in Proceedings of Second International Pyrotechnics Seminar, held at Snowmass-at-Aspen, Colorado, 20-24 July 1970. (Sponsored by Denver Research Institute, University of Denver, Denver, Colorado), p. 83. Available National Technical Information Service, 5285 Port Royal Road, Springfield, Virginia, 22161 - AD 913407

## EXPERIMENTAL\*

The formulas used in these experiments are given in Table 1. All materials were standard Mil Spec materials. The average magnesium particle size was 375 microns. The boron particle size was approximately 1 micron. The barium nitrate, polyvinyl chloride, and hexachlorobenzene particle sizes were not measured but all were less than 400 microns. The binder was a mixture of Dow epoxy resin, CX 7069.7, and a polyamine, CX 3482.1, in a ratio CX 7069.7 - 80% and CS 3482.1 -20%.

After mixing, the compositions were pressed into fishpaper tubes at  $5.62 \times 10^7 \text{ N/m}^2$  (8000 psi). The tubes had been coated with the binder mixture twenty-four hours prior to pressing. One hundred and fifty grams of composition were used for each candle. The finished candles were 4.4 centimeters (cm) in diameter and 5.5 cm long.

The flares were burned facedown at a distance of 1000 cm from the radiometers and 400 cm from the spectrographs. The radiometers are fitted with filters such that the filter + detector response curves match as closely as possible the CIE color-matching functions  $\bar{x}$ ,  $\bar{y}$ , and  $\bar{z}$ . Measurements from each detector then give the tristimulus values X, Y, and Z from which the chromaticity coordinates, x and y, can be calculated. The values of dominant wavelength and purity are then determined by the standard graphical method after plotting the chromaticity coordinates on a chromaticity diagram.<sup>2</sup> The radiometer which gives the tristimulus value of Y is calibrated against an NBS traceable standard lamp to give the values of luminous power.

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\* In order to specify procedures adequately, it has been necessary occasionally to identify commercial materials and equipment in this report. In no case does such identification imply recommendation, endorsement, or criticism by the Navy, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.

2. G. Wysecki and W. S. Stiles, Color Science: Concepts and Methods Quantitative Data and Formulas (John Wiley and Sons, Inc., NY, 1967).



TABLE 1. EXPERIMENTAL DATA

	<u>CO-30</u>	<u>CO-12</u>	<u>CO-13</u>	<u>CO-14</u>	<u>CO-15</u>	<u>CO-16</u>	<u>CO-18</u>	<u>CO-19</u>	<u>CO-20</u>
Mg	21	40	33	25	35	39	30	25	40
B	-	15	12	15	5	6	10	10	10
Ba(NO <sub>3</sub> ) <sub>2</sub>	22.5	40	50	55	55	50	50	50	40
KClO <sub>4</sub>	32.5	-	-	-	-	-	-	-	-
Cu	7	-	-	-	-	-	-	-	-
C <sub>6</sub> Cl <sub>6</sub>	-	-	-	-	-	-	5	10	5
PVC	12	-	-	-	-	-	-	-	-
Binder	5	5	5	5	5	5	5	5	5
Candlepower (kcd)	12.2	47.8	59.9	59.5	63.4	71.7	44.6	25.7	29.0
Burn Time (sec)	42	20	19	19	23	23	23	26	29
Efficiency (cd sec/g)	3416	6363	7587	7537	9721	10,994	6839	4455	5607
Dominant Wavelength	562	553	554	554	552	554	555	554	554
Purity	58	58	47	47	53	52	55	60	60

Visible spectra were taken with a Spex 1802 one meter grating spectrograph equipped with a 600 groove/millimeter (mm) grating. The spectrograph was used in the first order where the dispersion is 1.65 nm/mm. The spectra were recorded on Kodak 103-F Spectroscopic Plates\*. The spectrograph was used with a Corning 0-52 filter for order separation and a 10 micrometer slit. The exposure times were two seconds. Spectra of a 200-watt quartz-iodine lamp were also taken to provide the calibration for film response.

The spectra were scanned and digitized on an Optronics S-2000 densitometer and the film density was converted to radiant power readings by standard techniques. For specific regions of interest very accurate scans of film density were made using a Joyce-Loebel Model 3CS densitometer. The instrument was used in the analog mode for better accuracy.

## RESULTS

The experimental results of this investigation are summarized in Table 1. Values are given for candlepower, burn time, luminous efficiency, dominant wavelength, and purity for each experimental composition. The results are averages of four to six flares burned. The average experimental error in luminous efficiency is  $\pm 7$  percent. The experimental error in the value of dominant wavelength is  $\pm 2$  percent and the error in the purity is  $\pm 5$  percent.

The colors observed during the flare burns were green to greenish-white. Compositions C0-12 to C0-20 gave comparable green colors of varying intensity. These colors all appeared to be better than C0-30, the Navy standard green flare formula.

The visible radiant power spectra for the standard Navy green formulation, C0-30, and the best new green composition, C0-16, are shown in Figures 1 and 2 respectively. These spectra are each normalized to a value of one at their maxima. The data in Table 1 indicate that the intensity of C0-16 is a factor of 7 more than C0-30. The spectra are taken from a two-second interval during a flare burn and are chosen as being representative of the entire group of

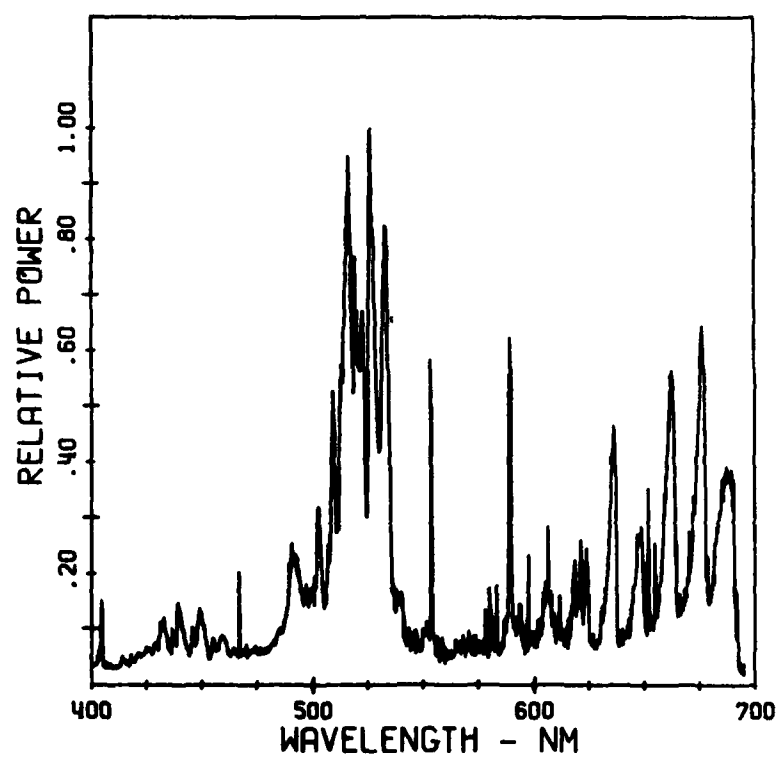


Figure 1. Radiant Power Spectrum of Standard Green Flare

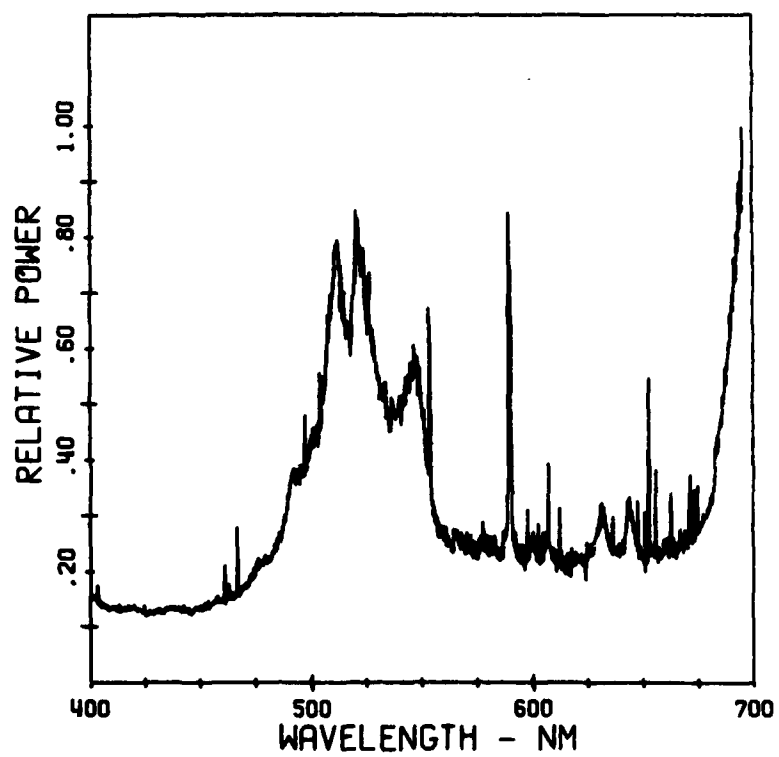


Figure 2. Radiant Power Spectrum of Improved Green Flare

spectra taken during these experiments. Little deviation was observed among spectra from different flares of the same formula type.

## DISCUSSION

The flares burned in these experiments fall into three basic categories: (1) those with boron, CO-12 - CO-16; (2) those with boron and a chlorine source, CO-18 - CO-20; and (3) the standard flare without boron, CO-30. The results indicate that the use of boron, magnesium, and barium nitrate produces good green flares with excellent efficiencies. The excitation purity of these flares, CO-12 - CO-16, is around 50% which is less than the purity for the standard green. The dominant wavelength for the boron-containing flares is 80-100 Å shorter than for the standard green, making the boron flares much greener than the standard. The efficiencies are a factor of 2-3 more than the standard and the luminous intensities greater by a factor of 4-5.

The addition of 5-10% hexachlorobenzene to the boron-containing flares, CO-19 - CO-20, does not significantly change the dominant wavelength. The excitation purity of the hexachlorobenzene-containing flares is 60%, which is comparable to the standard green. The efficiencies are slightly higher than the standard.

The radiant power spectrum of standard Navy green flare is shown in Figure 1. The flare composition is designed to maximize the emission from the BaCl molecule to produce the desired green color. Molecular BaCl emission is superimposed on less intense, but equally important BaO, BaOH, and Ba<sub>2</sub>O<sub>2</sub> band emissions extending from 460 nm to 678 nm. This emission, coupled with an underlying continuum from hot solid particles, is the contributing factor to the loss of color purity in both this composition and in the boron-containing compositions, CO-12 - CO-20. Composition CO-30 also contains copper and the resulting CuCl emissions are observed from 412-470 nm.

The most interesting part of this spectrum are the emission bands at 624 nm, 636 nm, 648 nm, 662 nm, and 675 nm. These bands are a result of SrCl emission and are not a part of any barium atomic or molecular emission system

as previously reported.<sup>1</sup> The strontium is most likely present as an impurity in the barium nitrate. While emissions from impurity constituents are quite common in pyrotechnic flares, they are usually a negligible part of the total part. The most common impurity is sodium which seems to be present in almost all compositions. However, even with its excellent emission properties, as an impurity it seldom accounts for more than 1% of the total power. The molecular emission from SrCl in the case of this flare accounts for almost 22% of the total radiant power. It should also be pointed out that this SrCl emission is not an isolated event but is observed in all compositions containing barium nitrate and a chlorine donor.

In the boron flares, Figure 2, the primary emission is from the boric acid fluctuation bands systems,  $\text{BO}_2$ , with maxima at 452 nm, 471 nm, 493 nm, 518 nm, 545 nm, and 580 nm. These bands are overlapped by the BaO/BaOH system. The increased flame temperatures of CO-12 - CO-16 when compared to the standard green, CO-30, account for the increased intensity. The increased efficiency is probably a result of the boron oxides being better emitters than the BaCl. The shorter dominant wavelength in the boron flares is due to the absence of the SrCl molecular emission in the red region of the spectrum. The lower purity is due to the increased emission in the background continuum - a result of the solid particles being at a higher temperature.

When the chlorine source is added, the emission is a result of BaCl, BaO, BaOH, and  $\text{BO}_2$ . The efficiency does not decrease drastically with  $\text{C}_6\text{Cl}_6$ . The improvement in purity when compared with CO-30 is due to added emissions in the green from  $\text{BO}_2$  and a reduced background continuum due to the lower temperatures. The SrCl emissions in the red region of the spectrum are present in the CO-18 - CO-20 formulas. The spectrum from this group of flares is not presented but is essentially an addition of Figures 1 and 2. The very intense  $\text{BO}_2$  fluctuation bands are superimposed on the BaCl bands and most of the structure of the BaCl bands is lost.

To get some idea of what these increases in candlepower mean, calculations were done by the method described by Middleton<sup>3</sup> to determine range of visibility of a colored signal. These results are summarized in Table 2. The meteorological ranges were assumed to be 5, 10, and 20 miles. The target distances were then determined for flares of 300, 20,000, and 70,000 cd at illumination levels of  $10^3$ ,  $10^0$ , and  $10^{-4}$  ft-cds. A level of  $10^3$  corresponds to a clear day,  $10^0$  to twilight, and  $10^{-4}$  to starlight. At the lowest level of illumination on a clear starlight night, a 70,000 cd flare can be seen twice as far as a 300 cd flare. However, under daylight conditions - not a situation where flares are now used - the 70,000 cd flare should be visible at ranges of 13,000 yards, while the 300 cd flare is visible only for 1700 yards. This of course assumes an ideal situation where the observer knows the location of the source. Effects of atmospheric scattering and color shifts have not been considered in this calculation. Thus it is conceivable that the higher efficiency green flares could be used as day signals.

#### CONCLUSIONS

Green flares have been demonstrated which retain acceptable dominant wavelength and purity and produce efficiencies of 6000 - 11,000 cd-s/g. The emission from these flares comes from a combination of molecular emission from  $\text{BO}_2$ ,  $\text{BO}$ ,  $\text{BaO}$ , and  $\text{BaOH}$ . While the purity of these signals is not as good as other flares which contain chlorine sources for the formation of  $\text{BaCl}$ , the dominant wavelength is shorter (as much as 100 Å in the case of a comparison with a standard green flare) making the flares appear less yellow.

Previously misidentified band structure in the red region of the spectra of flares containing barium nitrate and a chlorine source are now identified as emission from  $\text{SrCl}$ . The strontium is present only as an impurity in the barium; yet the emission from  $\text{SrCl}$  accounts for more than 20% of the total radiant power. If this emission could be eliminated (for example, by the use of ultrapure barium nitrate), the color purity of current green flares could be improved significantly.

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3. W. E. K. Middleton, Vision Through the Atmosphere (University of Toronto Press, Canada, 1952).

TABLE 2. CALCULATED RANGES

Met. Range (yds)	Illuminance Level (ft-cds)		
	$10^3$	$10^0$	$10^{-4}$
Intensity = 300 cp			
8800	1400	7500	13,500
17,600	1600	11,600	22,000
35,200	1700	16,800	35,000
Intensity = 20,000 cp			
8800	4900	14,200	21,000
17,600	7000	24,000	36,000
35,200	8800	38,000	61,000
Intensity = 70,000 cp			
8800	6500	16,500	23,000
17,600	9500	28,000	41,000
35,200	13,000	48,000	70,000



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